Experimental Diversion of Acid Mine Drainage and the Effects on a Headwater Stream

By Dev K. Niyogi, Diane M. McKnight, William M. Lewis, Jr., and Briant A. Kimball

ABSTRACT

An experimental diversion of acid mine drainage was set up near an abandoned mine in Saint Kevin Gulch, Colorado. A mass-balance approach using natural tracers was used to estimate flows into Saint Kevin Gulch. The diversion system collected about 85 percent of the mine water during its first year of operation (1994). In the first 2 months after the diversion, benthic algae in an experimental reach (stream reach around which mine drainage was diverted) became more abundant as water quality improved (increase in pH, decrease in zinc concentrations) and substrate quality changed (decrease in rate of metal hydroxide deposition). Further increases in pH to levels above 4.6, however, led to lower algal biomass in subsequent years (1995-97). An increase in deposition of aluminum precipitates at pH greater than 4.6 may account for the suppression of algal biomass. The pH in the experimental reach was lower in 1998 and algal biomass increased. Mine drainage presents a complex, interactive set of stresses on stream ecosystems. These interactions need to be considered in remediation goals and plans.

INTRODUCTION

Acid mine drainage has created water-quality concerns worldwide for many years. Remediation activities are currently being implemented at many sources of mine drainage with the goal of improving water quality and promoting ecological recovery in receiving streams. This report describes a study of Saint Kevin Gulch, a headwater stream near Leadville, Colorado, where mine drainage was experimentally diverted from the stream to simulate conditions that might develop following remediation of the site. The characteristics of Saint Kevin Gulch are similar to other streams that are part of the U.S. Geological Survey (USGS) Abandoned Mine Lands Initiative. The studies at Saint Kevin Gulch can be used in selecting well-informed options for remediation at many of these sites. This report describes two data sets: (1) use of a natural tracer to estimate flows associated with the diversion system, and (2) analysis of algal biomass to assess the degree of stream recovery after the diversion.

A natural tracer can be used to quantify flows that are difficult to measure directly. This method uses changes in concentrations of chemicals across inflows to estimate flow rates. Two main requirements are needed for a natural

tracer approach to be effective (Bencala and others, 1987). First, the tracer chemical must behave conservatively within the stream reach of interest. Second, there must be a difference in concentration of the tracer between the stream and the inflow. The greater the difference in the concentration, the better is the resolution of the estimates of flow. Bencala and others (1987) used a natural tracer to study flows and solute transport at the confluence of an acidic and a neutral stream in Colorado. Bencala and Ortiz (1999) describe results from a natural (ambient) tracer study in Wightman Fork, a stream in south-central Colorado.

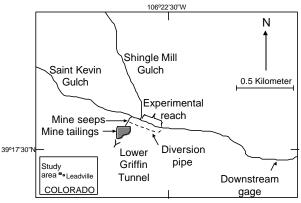
Acid mine drainage affects the aquatic biota by three main mechanisms (McKnight and Feder, 1984; Kelly, 1988): (1) acidity, (2) toxic concentrations of dissolved metals, and (3) precipitation of metal hydroxides (mainly iron and aluminum hydroxides). While many studies have described the effects of mine drainage on aquatic biota (reviewed in Kelly, 1988), information on the recovery of streams from mine drainage is limited (Chadwick and others, 1986; Nelson and Roline, 1996).

Saint Kevin Gulch currently receives acid mine drainage from several abandoned mines in the watershed. During the summer of 1994, the USGS

set up an experimental diversion at one abandoned mine site to evaluate the potential effects of remediation on water quality and biota in the stream. Metal concentrations in the stream were measured to monitor changes in water quality and to quantify inflows by use of a natural-tracer approach. Algal biomass was quantified in the experimental reach, the stream reach around which mine drainage was diverted, as an indicator of ecological recovery. Niyogi and others (in press) reported data on algal biomass from the first 3 years of this experiment. This report summarizes data for an additional 2 years.

SITE DESCRIPTION

Saint Kevin Gulch is a headwater stream in Lake County, Colorado, near the town of Leadville (fig. 1). The stream starts near the Continental Divide and flows into Tennessee Creek, which then flows into the upper Arkansas River. The stream currently receives acid drainage from two abandoned mines and several smaller seeps. This



study focused on the lower mine, the Lower Griffin Tunnel, which is the main source of acidity and dissolved metals to the stream.

Figure 1. Map of Saint Kevin Gulch study area.

Several small seeps of acid mine drainage emanate from the base of a tailings pile at the lower Griffin mine and flow into Saint Kevin Gulch. Shingle Mill Gulch, a minimally affected tributary, joins Saint Kevin Gulch just downstream from the mine. On July 27, 1994, mine drainage from these seeps was collected into a plastic pipe and diverted to a point about 100 meters downstream from the original inflows (fig. 1). The reach between the Shingle Mill Gulch confluence and the end of the

diversion pipe is referred to as the "experimental reach."

The chemistry and biology of Saint Kevin Gulch has been studied previously. Kimball and others (1994) quantified hydrologic and chemical reaction rates in the stream by use of a tracer injection experiment. Broshears and others (1996) performed an experimental addition of sodium carbonate to study chemical reactions under increased pH. McKnight (1988) and Tate and others (1995) have studied the algal communities in Saint Kevin Gulch and their interactions with phosphate.

METHODS

The natural tracer approach used in this study is based on a simple chemical mass balance. Assuming that a given solute behaves conservatively, solute mass balance is

$$C_1 Q_1 + C_t Q_t = C_2 Q_2$$
 (1)

where

 C_1 and Q_1 are the concentration and flow for the upstream site (upstream from tributary).

 C_t and Q_t are the concentration and flow for a tributary that enters the stream, and

 C_2 and Q_2 are the concentration and flow for the downstream site (downstream from tributary).

The downstream flow (Q_2) equals the two input flows $(Q_1$ and $Q_t)$, assuming that there is no net loss or gain of water within the reach. Therefore,

$$C_1(Q_2 - Q_t) + C_t Q_t = C_2 Q_2$$
 (2)

Equation 2 can be used to calculate the flow of the tributary given the three concentrations of the tracer and the downstream flow. In 1994, a gage was operated at a downstream site in Saint Kevin Gulch, about 1.2 kilometers downstream from the mine. With this measured flow and measured solute concentrations (for both stream and tributary sites), flows for tributaries into Saint Kevin Gulch were calculated successively, progressing upstream from the gage site to the mine site.

Upstream from the downstream site (and gage location), flows were calculated for the following inflows (fig. 2): (1) metal-free ground water between the end of diversion pipe and the downstream gage, (2) the flow from the diversion pipe, (3) metal-rich ground water between Shingle Mill Gulch and the diversion pipe, (4) Shingle Mill Gulch, and (5) mine drainage from the seeps (before and after setup of the collection system). The main goal was to compare the flows from the diversion pipe with the remaining ground-water inflow from the mine drainage seeps.

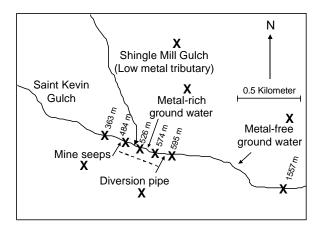


Figure 2. Sampling sites in Saint Kevin Gulch, Colo., for natural-tracer estimation of tributary flows. Arrows indicate inflows to Saint Kevin Gulch. X indicates sites used in natural-tracer estimation of flows. Saint Kevin Gulch sites are labeled as distance (in meters) from an upstream reference point.

A variety of dissolved ions were considered for use as the conservative solute in the flow calculations. Based on a review of the data and previous studies (Bencala and others, 1987; Kimball and others, 1994), dissolved manganese and zinc were selected as conservative tracers for this study. These ions are predicted to behave conservatively in the stream; that is, the ions are not subject to reactions that alter their concentrations. Some ions, such as iron and aluminum, undergo precipitation reactions in the stream and were not used for this reason. Chemical equilibrium models predict that both manganese and zinc should be present as dissolved species in the low pH waters of Saint Kevin Gulch. Moreover, other studies (Smith and others, 1991: Webster and others, 1998) have predicted that manganese and zinc ions $(Mn^{2+} \text{ and } Zn^{2+})$ are not

readily adsorbed onto suspended solids in the stream (primarily iron and aluminum hydroxides) in the low-pH waters of Saint Kevin Gulch.

Water samples were collected from sites along Saint Kevin Gulch throughout 1994 during ice-free periods (May through October). Both raw (unfiltered) and filtered (0.1 micrometer) samples were collected, acidified, and analyzed for metals by inductively coupled argon plasma atomic emission spectroscopy (Kimball and others, 1994). Samples were collected from six locations along Saint Kevin Gulch (fig. 2), from Shingle Mill Gulch, and from the outlet of the diversion pipe. Mine drainage from the seeps was assumed to have the same manganese and zinc concentration as the diversion pipe water. For the metal-rich ground water downstream from Shingle Mill Gulch, a ground-water chemistry sample was used from a previous study (B.A. Kimball, USGS, unpub. data). Finally, ground water entering Saint Kevin Gulch between the diversion pipe and the downstream gage was assumed to contain neither manganese nor zinc.

Tracer concentrations from raw and filtered samples were usually similar (within 5 percent), as expected from the chemical model predictions indicating little reactivity, as mentioned previously. For most samples, concentrations of manganese and zinc from filtered samples were used in the analyses for flow calculations. In some cases concentrations from raw samples were used because of discrepancies with the data for filtered samples resulting from possible sampling or analytical error. Flow estimates from manganese and zinc concentrations were averaged to determine the final estimate. During each sampling, flow at the end of the diversion pipe also was measured directly with a bucket and stopwatch.

The diversion was maintained during base-flow conditions from 1994 to 1998. In addition to water-quality measurements (pH, dissolved metals), the deposition rate of metal hydroxides and amount of benthic algae growing in the experimental reach were also monitored. The rate of metal hydroxide deposition was measured by placing rocks in the stream and determining the ash mass of deposited material on the rock after several weeks (see Niyogi and others [in press] for more details). Rocks were placed in riffles but not in the few pools along the stream reach. Results are presented as ash mass of material per unit area of

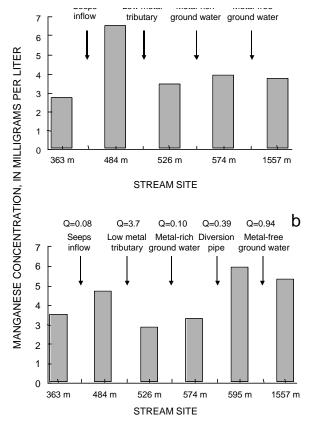
streambed per time. Algal biomass in the experimental reach was measured during late summer base flow (early September). Detailed methods for algal sampling are presented in Niyogi and others (in press). Rocks from the stream were collected and algae were scraped off and filtered onto a glass-fiber filter. Filters and algae were extracted by use of a hot ethanol extraction, and chlorophyll-*a* content was determined (Lewis and others, 1984). Results are presented as milligrams of chlorophyll *a* per square meter of streambed.

RESULTS

Natural Tracer Estimation of Mine Drainage Flows

Concentrations of manganese and zinc proved reliable for use as natural tracers in Saint Kevin Gulch. As an example, figure 3a shows the downstream gradient in manganese concentrations for samples collected on July 20, 1994, before the mine-drainage diversion was set up. Manganese was present at less than 3 milligrams per liter (mg/L) at a site (363 m) located just upstream from the mine tailings. The main seeps at the mine caused the stream manganese concentration to increase to more than 6 mg/L. Shingle Mill, a relatively uncontaminated tributary of similar flow to Saint Kevin Gulch, joined the stream and caused a decrease in manganese concentration to less than 4 mg/L. Metal-rich ground water then caused a slight increase in manganese concentration in the stream upstream of the

Figure 3. Downstream profile of dissolved manganese concentrations along Saint Kevin Gulch, Colo., before (a) and after (b) diversion system was established. Sites along Saint Kevin Gulch are labeled as distances, in meters, from an



upstream reference point. Inflows are listed between stream sites. Estimated flows (Q) are presented in liters per second.

diversion outflow. Finally, inflow of relatively uncontaminated ground water over the next kilometer of stream decreased the manganese concentration to 3.8 mg/L at site 1557 m.

Figure 3b shows a similar downstream gradient in manganese concentrations on September 4, 1994, after the diversion system was established. There were still some acidic inflows, through ground water, into the stream from the mine, which caused an increase in manganese concentration. The diversion pipe released the acid mine drainage between the 574 m and 595 m sites, where the manganese concentration increased from 3.3 mg/L to 5.9 mg/L. As before, ground-water inflows diluted the manganese concentration in the stream at the downstream site (1557 m).

The estimated flows for the mine drainage seeps and diversion pipe are shown in figure 4. The earliest sampling date (June 21, 1994) had the highest flow of the mine drainage seeps, as expected, with snowmelt. Calculated flows from the diversion pipe were validated with direct measurements; estimates and direct measurements were always within 10 percent of each other. The mean percentage of mine drainage collected by the system in 1994 was 85 percent (standard deviation = 4 percent; n = 6 sampling dates).

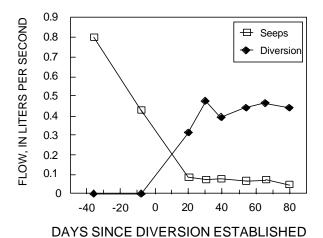
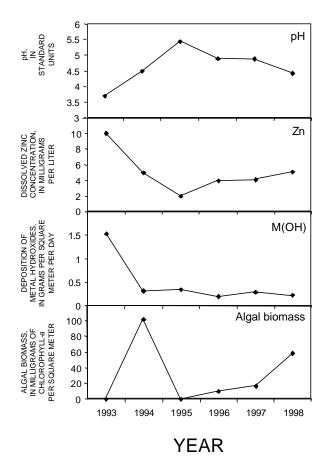


Figure 4. Estimated flows of acid mine drainage from seeps at mine and from diversion pipe. Day 0 is when the diversion system was established, July 27, 1994.

Effects of Diversion on Experimental Reach

Water quality improved substantially in the experimental reach after operation of the diversion system began. The pH and dissolved zinc concentrations for base-flow conditions (early September) from 1993 to 1998 are presented in figure 5. The pH increased from 3.7 during base flow in 1993 (prior to diversion) to 4.5 in 1994. In 1995, the pH increased to 5.4, due partly to increased flow in the stream from a large snowpack that year. The pH was about 4.9 in 1996 and 1997 and was lower (4.4) in 1998. Dissolved zinc concentrations showed a related trend. Lower concentrations of zinc were

Figure 5. Characteristics of the experimental reach in the year before (1993) and the 5 years after the diversion (established in 1994). Reported values are from samples collected during late



summer (early September) base flow. M(OH) refers to deposition rate of metal hydroxides.

measured after the diversion was constructed, and the lowest measured concentration was in 1995.

The deposition rate of metal hydroxides in the experimental reach decreased substantially after the diversion (fig. 5). Differences among the years after the diversion (1994 to 1998) were slight. Algae attained high biomass in 1994, more than 100 milligrams chlorophyll-a per square meter (mg chl a/m^2) just after the diversion was set up (fig. 5). During the following 3 years, however, algal biomass in the experimental reach was lower and never exceeded 20 mg chl a/m^2 . Algal biomass was higher (62 mg chl a/m^2) in 1998.

DISCUSSION

Natural Tracer Estimation of Mine Drainage Flows

The natural tracer method using manganese and zinc concentrations proved feasible for determining rates for inflows to Saint Kevin Gulch. This simple mass-balance approach for estimates of flow from the diversion pipe compared well with direct measurements. However, there are two main problems in this approach as presented here. First, manganese and zinc may be reactive to some extent in the streams as opposed to being strictly conservative. Kimball and others (1994) modeled manganese concentrations in Saint Kevin Gulch and found that manganese was lost from the streamwater in one small reach. Zinc may also be slightly reactive, as the pH in the experimental reach was approaching values where zinc will sorb to metal hydroxides (Webster and others, 1998).

The second limitation of our natural tracer approach is in estimating ground-water fluxes in the downstream reach of Saint Kevin Gulch. It was assumed that this ground water contained no manganese or zinc. In reality, however, there are some seeps with significant concentrations of metals (Kimball and others, 1994). The complex spatial distribution of ground water with varying chemistry makes the resolution of these groundwater flows difficult, and estimates for these flows would be less reliable than other estimates from more discrete sources. Kimball and others (1994) reported a more intensive sampling effort designed to quantify inflows and instream reactions along Saint Kevin Gulch during a tracer injection experiment. Kimball and others (1994) overcame the limitation of a natural tracer approach by adding lithium, which is not present in significant concentrations in the stream or ground water, and by measuring dilution to calculate inflows.

The tracer aspect of the study was used to determine the percentage of mine drainage collected using a simple system of pipes and trenches. Based on six flow estimates from late summer of 1994, it is estimated that approximately 85 percent of the mine drainage from the abandoned mine was collected by the diversion system. The remaining 15 percent of the mine drainage enters the stream near the mine as subsurface flow and leaks in the diversion system.

Effects of Diversion on Experimental Reach

Before the diversion, in 1993, the reach downstream from Shingle Mill Gulch had a pH of 3.7, a zinc concentration of 10 mg/L, and a deposition rate of metal hydroxides of 1.5 grams per square meter per day (g m⁻² d⁻¹). Very little algae accumulated during the summer in this reach

of Saint Kevin Gulch. As expected, the diversion created an experimental reach with increased pH and lower concentrations of dissolved zinc. The experimental reach also had lower rates of metal hydroxide deposition onto the streambed (fig. 5).

Differences in the water quality of the experimental reach during the 5 years following the diversion (1994 to 1998) were observed. These differences could be due to changes in streamflow, altered water chemistry from upstream because of a treatment system at another mine in the watershed, and changes in the mine-drainage flows and collection system at the lower Griffin mine. Thus, a high flow in 1995 from a large snowpack likely caused a higher pH (5.4) and a lower concentration of dissolved zinc (2 mg/L) in the experimental reach. In 1998, low flow in the stream and an increase in uncollected flows of mine drainage likely caused a low pH (4.4) in the experimental reach.

The response of algal communities to the diversion was complex and varied from year to year. Algae attained high biomass in the experimental reach in 1994 and 1998. There was much less algal biomass in 1995, 1996, and 1997. The pH in the experimental reach was highest and zinc concentrations were lowest during 1995-97, the years with lowest algal biomass. Changes in the rate of metal hydroxide deposition during 1995-97 were modest. The rate of metal hydroxide deposition in the experimental reach was similar to that in a downstream, reference reach, which had high biomass of algae throughout the study (Niyogi and others, in press).

The main difference between the years of high accumulation of algal biomass and low accumulation was a change in the composition of metal hydroxides that were deposited onto the streambed. During 1995-97, the pH in the experimental reach increased to the point at which aluminum hydroxides or other aluminum compounds (Broshears and others, 1996) precipitated out of solution and were deposited onto the streambed (Niyogi and others, in press). Aluminum compounds, including hydroxides and other more complex compounds, typically precipitate at a pH above 4.6 (Nordstrom and Ball, 1986). In 1994 and 1998, the pH remained less than 4.6, and iron hydroxides were the predominant metal compounds deposited. During 1994-98, there were no differences in other factors that might control algal abundance, such as

concentrations of nutrients or densities of grazing invertebrates (unpub. data).

It is unclear why algae in the stream (predominantly *Ulothrix* sp.) did not grow as well in areas where aluminum hydroxides were deposited (Nivogi and others, in press). Other ecological indicators, such as invertebrate communities and rates of leaf decomposition, had similar responses in the experimental reach (unpub. data). Despite the higher pH and lower zinc concentrations in the experimental reach, ecological recovery was limited by metal hydroxide deposition, including a change from iron to aluminum compounds in the deposited material. With mine drainage, improved water quality may thus lead to changes in the physical habitat that control ecological responses. Similar patterns have been seen in other streams in Colorado, such as the Snake River (McKnight and Feder, 1984). Wightman Fork, Gamble Gulch, and the Animas River (unpub. data). Other studies also have documented the physical effects of metal hydroxide deposition (Sode, 1983; Robbins and others, 1997).

The interactions between water quality and substrate quality highlight the complex effects of acid mine drainage. Metal hydroxides and other metal compounds remain soluble at low pH but precipitate at higher pH and can coat streambeds. As highly acidic waters increase in pH through buffering or dilution, a stage of precipitation and deposition of iron and then aluminum hydroxides will occur before the waters reach neutral pH. Although low pH and high concentrations of dissolved metals affect aquatic life, the deposition of metal hydroxides can result in more pronounced effects on the biomass of stream biota and ecological processes. Failure to consider the role of precipitation of metal hydroxides can prevent successful prediction of ecological recovery in streams undergoing remediation.

REFERENCES

- Bencala, K.E., McKnight, D.M., and Zellweger, G.W., 1987, Evaluation of natural tracers in an acidic and metal-rich stream: Water Resources Research, v. 23, no. 5, p. 827-836.
- Bencala, K.E., and Ortiz, R.F., 1999, Theory and(or) reality--Analysis of sulfate mass-balance at Summitville, Colorado, poses process questions about the estimation of metal loadings, *in* Morganwalp, D.W., and Buxton,

- H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999--Volume 1--Contamination from Hardrock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, this volume.
- Broshears, R.E., Runkel, R.L., Kimball, B.A., McKnight, D.M., and Bencala, K.A., 1996, Reactive solute transport in an acidic stream-experimental pH increase and simulation of controls on pH, aluminum, and iron: Environmental Science and Technology, v. 30, p. 3016-3024.
- Chadwick, J.W., Canton, S.P., and Dent, R.L., 1986, Recovery of benthic invertebrate communities in Silver Bow Creek, Montana, following improved metal mine wastewater treatment: Water, Air, and Soil Pollution, v. 28, p. 427-438.
- Kelly, M., 1988, Mining and the freshwater environment: New York, Elsevier Science Publishers, 231 p.
- Kimball, B.A., Broshears, R.E., Bencala, K.E., and McKnight, D.M., 1994, Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage: Environmental Science and Technology, v. 28, p. 2065-2073.
- Lewis, Jr., W.M., Saunders III, J.F., Crumpacker, Sr., D.W., and Brendecke, C.M., 1984, Eutrophication and land use: New York, Springer-Verlag, 202 p.
- McKnight, D.M., 1988, Metal-tolerant algae in Saint Kevin Gulch, Colorado, U.S. Geological Survey Open-File Report 87-764, p. 113-117.
- McKnight, D.M., and Feder, G.L., 1984, The ecological effect of acid conditions and precipitation of hydrous metal oxides in a Rocky Mountain stream: Hydrobiologia, v. 199, p.129-138.
- Nelson, S.M., and Roline, R.A., 1996, Recovery of a stream macroinvertebrate community from mine drainage disturbance: Hydrobiologia, v. 339, p. 73-84.
- Niyogi, D.K., McKnight, D.M., and Lewis, Jr., W.M., in press, Influences of water and substrate quality for periphyton in a montane stream affected by acid mine drainage: Limnology and Oceanography.
- Nordstrom, D.K., and Ball, J.W., 1986, The geochemical behavior of aluminum in acidified surface water: Science, v. 232, p. 54-56.

- Robbins, E.I., Anderson, J.E., Cravotta, C.A., Bilger, M.D., Desmond, G.B., Earle, J.I., Flohr, M.J.K., Jordan, B.M., Krishnaswamy, Rama, Nord, G.L, Jr., Seal, R.R., II, and Snyder, C.D., 1997, AMD flocculates and precipitates--Potential for habitat destruction by sediment of a different color: U.S. Geological Survey Sediment Workshop, Harpers Ferry, W.Va., 12 p.
- Smith, K.S., Ranville, J.F., and Macalady, D.L., 1991, Predictive modeling of copper, cadmium, and zinc partitioning between streamwater and bed sediment from a stream receiving acid mine drainage, Saint Kevin Gulch, Colorado, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program-Proceedings of the technical meeting, Monterey, Calif., March 11-15, 1991: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 380-386.
- Sode, A., 1983, Effect of ferric hydroxide on algae and oxygen consumption by sediment in a Danish stream: Archives fur Hydrobiologia Supplement, v. 65, p. 134-162.
- Tate, C.M., Broshears, R.E., and McKnight, D.M., 1995, Phosphate dynamics in an acidic mountain stream--Interactions involving algal uptake, sorption by iron oxide, and photoreduction: Limnology and Oceanography, v. 40, p. 938-945.
- Webster, J.G., Swedlund, P.J., and Webster, K.S., 1998, Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulfate: Environmental Science and Technology, v. 32, no. 10, p. 1361-1368.

AUTHOR INFORMATION

Dev K. Niyogi, U.S. Geological Survey, Denver, Colorado, and University of Colorado, Boulder, Colorado (niyogi@colorado.edu)

Diane M. McKnight and William M. Lewis, Jr., University of Colorado, Boulder, Colorado

Briant A. Kimball, U.S. Geological Survey, Salt Lake City, Utah